

Transport properties and thermal studies on pure and Cu^{2+} -doped potassium hydrogen maleate single crystals

A D REDDY, S G SATHYANARAYAN and G S SASTRY

Department of Physics, University College of Science, Osmania University,
Hyderabad 500007, India

MS received 13 June 1983; revised 9 December 1983

Abstract. Conductivity, thermally stimulated depolarisation (TSDC) and thermal studies are carried out on pure and Cu^{2+} -doped potassium hydrogen maleate single crystals. Both DTA and DSC reveal first-order phase transition at 503 K. DSC further shows that the crystal decomposes even before the transition is complete. A 'knee' is observed around 505 K in conductivity plots at this transition. The TSDC of Cu^{2+} -doped system gave a single peak at 241 K and the reasons are analysed. Activation energies from conductivity and TSDC suggest proton conduction. However no direct evidence in coulometric experiment could be observed. But thermoelectric power measurements reveal the charge carriers to be positive.

Keywords. Electrical conductivity; thermally stimulated depolarisation currents; phase transition; activation energy; frequency factor; potassium hydrogen maleate.

1. Introduction

Potassium hydrogen maleate (KHM), $\text{K}^+ (\text{OOC.CH}=\text{CH.COOH})^-$ is an acid salt of maleic acid. Infrared spectra (Cardwell *et al* 1953) showed that the intramolecular hydrogen bond in the hydrogen maleate ion (HM^-) is stronger than in maleic acid. The hydrogen bond is very short *i.e.* 2.40 ± 0.02 Å (Shahat 1952) and symmetrical (Cardwell *et al* 1953) in HM^- ion, as shown in figure 1. Chandra Mouli and Sastry (1982) reported ESR studies on $\text{KHM}:\text{Cu}^{2+}$ recently indicating that Cu^{2+} ion enters the lattice interstitially. In this paper, the transport properties and thermal studies on pure as well as Cu^{2+} -doped KHM single crystals are reported.

2. Growth and crystal structure

Potassium hydrogen maleate (KHM) is grown from aqueous solution containing potassium hydrogen carbonate and maleic acid. Few drops of copper sulphate are added to the solution for the growth of doped system, $\text{KHM}:\text{Cu}^{2+}$. The pure crystals are transparent, platy with (001) face and the doped ones are also platy but bluish in colour.

The crystal structure of KHM is reported by Darlow and Cochran (1961). It crystallises in orthorhombic space group Pbcm, with $a = 4.54$, $b = 7.78$, $c = 15.95$ Å, $z = 4$ and 1.82 g cm⁻³ density. This space group has earlier been proposed by Peterson and Levy (1958) from neutron diffraction study.

The structure of KHM consists of alternate layers of K^+ and HM^- ions, the anions

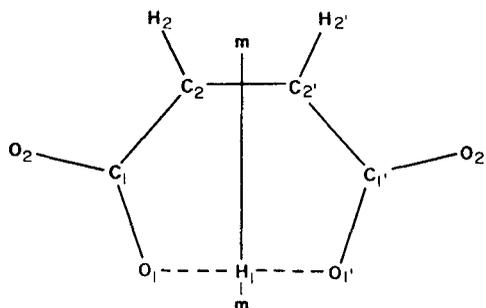


Figure 1. The HM^- ion showing the space group and mirror plane.

being oriented so that there are sheets of oxygens on either side of potassium layers. The K^+ ions are on diads parallel to the a -axis and HM^- ions are parallel to the c -axis.

3. Experimental details

Electrical conductivity was measured on pure and Cu^{2+} -doped KHM along the c -axis from 323 to 515 K using an experimental arrangement described by Madhusudan *et al* (1981). Thermoelectric power (TEP) was measured by the hot-probe method (Bruck *et al* 1969), maintaining a temperature difference of 30 K between hot and cold junctions. Thermally-stimulated depolarisation studies (TSDC) are carried out on $\text{KHM}:\text{Cu}^{2+}$ along the c -axis in a cell described earlier (Madhusudan *et al* 1981). A DC voltage of 250 V is applied on a specimen of 0.15 cm at room temperature for 20 min. It is then cooled to low temperatures and the TSDC currents are recorded while heating the specimen at a constant rate of $0.125^\circ \text{sec}^{-1}$.

The DTA thermogram was obtained using Leeds and Northrup unit at the sensitivity of $100 \mu\text{V}$ and 12.5 K min^{-1} heating rate, with α -calcina as the reference material. Differential scanning calorimetric (DSC) studies are carried out using Perkin-Elmer DSC II-B unit in nitrogen atmosphere. The heating rate was 20 K min^{-1} at 10 mcal sensitivity range.

4. Results and discussion

Electrical conductivity plots of pure and Cu^{2+} doped KHM along the c -axis are shown in figure 2. The plot of pure crystal shows two knees at 413 and around 505 K. The DTA and DSC thermograms shown in figures 3 and 4 respectively exhibit single peak at 503 K. This peak is endothermic and the temperature of transition is obtained by the intersection point of the tangents drawn to the trace at the onset of the transition (Daniels 1973). This transition is sharp and hence can be treated as a first-order transition. Therefore the knee at 505 K in the conductivity plot is attributed to the phase transition whereas the lower one at 413 K separates the intrinsic and extrinsic regions. The DSC thermogram further reveals that the system decomposes even before the transition is complete. The decomposition starts at about 526 K, which is marked by loss in weight of the sample. The sample emerges from the sample holder into the pan. Hence ΔH measurements are not valid. This is confirmed by repeated observations

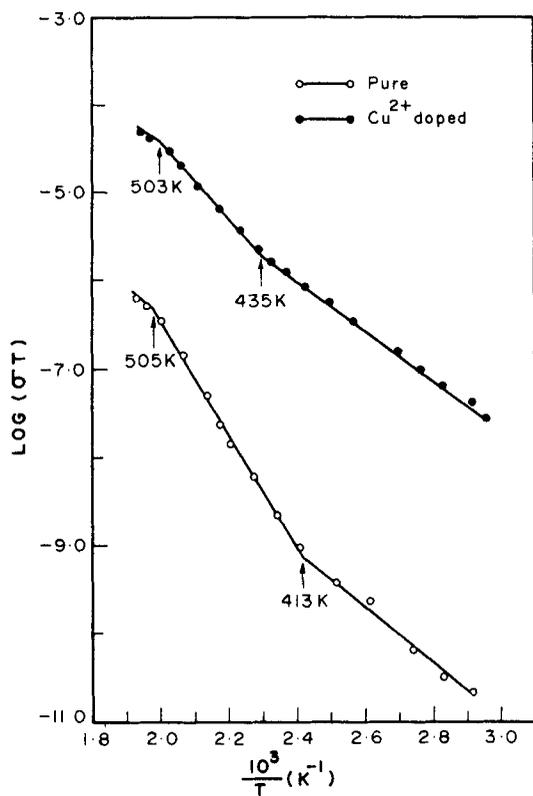


Figure 2. Conductivity plots of KHM single crystals along the *c*-axis.

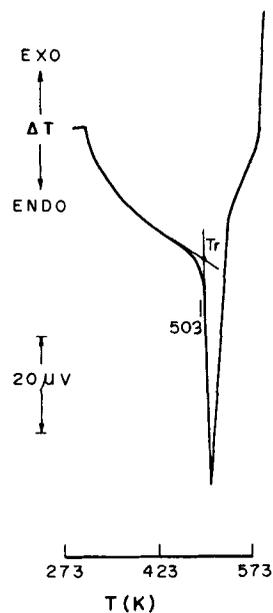


Figure 3. DTA thermogram of KHM.

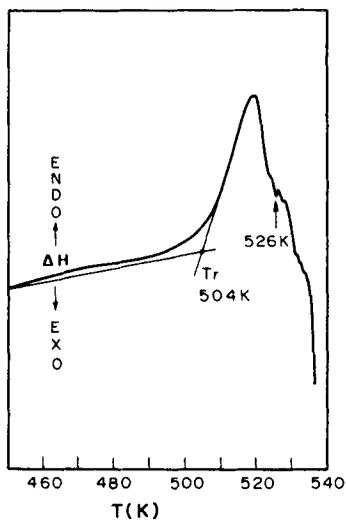


Figure 4. DSC heating curve of KHM at 10 mcal sec^{-1} sensitivity and 10 K min^{-1} heating rate. The weight of the sample was 18.85 mg.

with 10 and 20 K min⁻¹ heating rates. Further, the powder is brownish at the end of the DSC run.

The conductivity plot of Cu²⁺ doped KHM also shows similar knees at 435 and 503 K with at least two orders greater conduction than that of the pure one at all temperatures. Similar observations were made earlier on ADP and KDP crystals, when doped with different anions like SO₄²⁻, CrO₄²⁻, Cr₂O₇²⁻ or divalent cations like Ba²⁺ (Chowdari and Ravi Sekhar 1979; Murphy 1964). In all these cases it has been concluded that proton vacancies are formed for charge neutrality, and hence conduction increases, as protons are the charge carriers.

Recently it has been concluded from ESR studies that in KHM:Cu²⁺, the dopant enters the lattice interstitially (Chandra Mouli and Sastry 1982). These authors also suggested that the charge compensation is achieved by the release of two protons, positioned parallel to the *c*-axis. There are 12 such protons per unit cell in the system. Projection of KHM crystal structure on *ab*-plane along with Cu²⁺ location is given in figure 5.

The activation energies calculated using least-squares method in various regions of the pure and doped crystals are given in table 1, along with values for other hydrogen bonded systems. A comparison of these values with those of KHM indicates that protons might be the charge carriers in the crystal.

Thermoelectric power (TEP) studies performed on this system show that the sign of the charge carriers is positive. This also supports protons as the charge carriers in this system. A plot of Seebeck coefficient *Q*, against the temperature of the hot junction *T* is given in figure 6. The TEP decreases with increase in temperature of the hot junction.

4.1 TSDC studies

When an aliovalent impurity is doped into a crystal, a vacancy is formed to maintain charge neutrality. The impurity-vacancy (i-v) pair, thus formed, is held together by Coulombic forces, to form an electric dipole. These dipoles are oriented along the

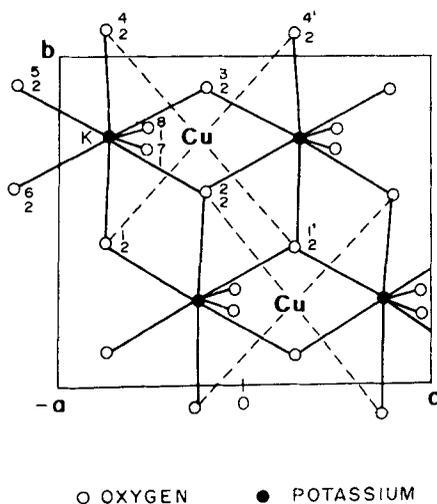
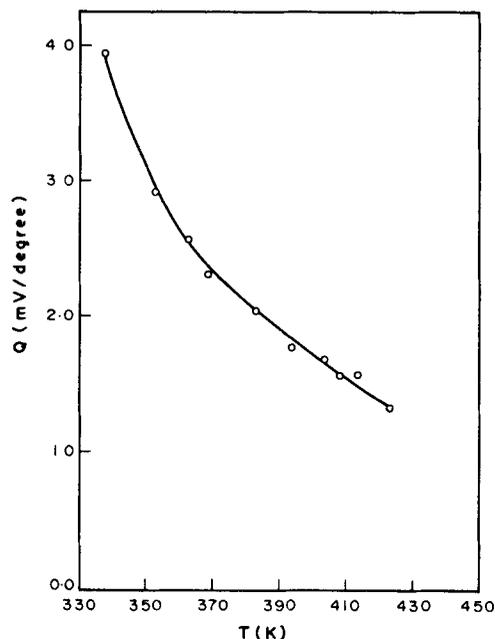


Figure 5. Projection of the crystal structure KHM in *ab*-plane and the location of Cu²⁺ ion (after Chandra Mouli and Sastry 1982).

Table 1. Activation energy from conductivity data along *c*-axis.

System	Temperature range	<i>E</i> (eV)	Reference
KHM pure	< 413	0.64	Present
	413 > <i>T</i> < 505	1.24	
	> 505	0.63	
KHM:Cu ²⁺	< 435	0.61	Present
	435 > <i>T</i> < 503	0.90	
	> 503	0.55	
ADP	303 > <i>T</i> < 363	0.70	Subhadra <i>et al</i> (1983)
	363 > <i>T</i> < 398	1.78	
ADP	—	0.61	Chowdari and Ravi Sekhar (1979)
KDP	< 453	0.55	
	> 453	0.80	
Li(N ₂ H ₅)SO ₄ :VO ²⁺	< 380	0.83	Reddy <i>et al</i> (1982a)
	> 380	0.65	

external field direction and are 'frozen-in' by cooling the system to low temperature. The field is then removed and the specimen is heated at a constant rate, typically at a rate of 0.1 K sec⁻¹. The electric dipole alters its orientation due to the thermal energy supplied and the defect jumps around the immobile impurity ion (Bucci *et al* 1966). Several methods are available in the literature for evaluation of activation energy *E*, and the frequency factor 1/τ₀ for the reorientation of 1-v dipoles (Radhakrishna and Haridoss 1978). Some of those that are used here are briefly described below.

**Figure 6.** Thermoelectric power vs temperature of hot junction of KHM pure crystal.

When a polarisation 'frozen-in' crystal is heated at a constant rate, the depolarisation current density is given by

$$J(T) = \frac{P_0}{\tau_0} \exp(-E/kT) \exp \left[-(b\tau_0)^{-1} \int_{T_0}^T \exp(-E/kT') dT' \right], \quad (1)$$

where P_0 is the initial polarisation, b the heating rate, E the activation energy for reorientation, and τ_0 the inverse frequency factor (Hor *et al* 1976).

Chen (1977) using the half-width w and T_m , the temperature at the maximum, found for the first order kinetics that

$$E = 2.52 \frac{kT_m^2}{w} - 2 kT_m. \quad (2)$$

Using this equation, the activation energy can be evaluated. Further, utilising the condition for maximum,

$$bE/kT_m^2 = \frac{1}{\tau_0} \exp(-E/kT_m). \quad (3)$$

τ_0 can be evaluated once E is known. Curve fitting is another method by which E and τ_0 can be obtained. Squire's (1970) approximation for the rc integral in (1) is used to calculate the currents. A TDC-12 computer with Fortran-II is used to compute the values from Squire's (1970) approximation.

Balarin (1975) constructed a nomogram for the direct evaluation of activation energy provided the half-width and peak temperature of the glow-curve are known.

TSDC studies of crystals at phase transition can be made even in pure systems (Winter and Rossler 1976; Reddy *et al* 1983). In cases where these currents are of measurable value, the glow curve can be recorded and analysed. In KHM , the transition occurs at 503 K, and hence these studies cannot be made. In addition TSDC currents are overshadowed by much larger conduction currents because of the high conduction of the system at these elevated temperatures. Therefore a Cu^{2+} -doped KHM is chosen to observe TSDC peaks. The activation energy required for reorientation of I-V dipoles is measured from this data. If this gives the same value as that obtained from the conductivity, it can be inferred that the transport mechanism is due to the ions forming vacancies in doped system.

TSDC spectrum of $\text{KHM}:\text{Cu}^{2+}$ is given in figure 7 along with the theoretical curve. The experimentally observed curve slowly increases at the lower part and reaches the maximum at 241 K. It then decreases to more than 70% of its peak value, but never drops to zero. Although the theoretical and experimental TSDC curves do not coincide at the lower parts, they superimpose for most part of the spectrum. The form-factor pertaining to the spectrum is 0.43 which indicates the peak to be of the first-order (Chen 1977). The single peak thus observed is analysed by various methods and the activation energies and frequency factor obtained are tabulated in table 2. The close agreement of activation energies both from conductivity and TSDC experiments suggests that the peak is due to I-V dipole reorientation.

It is surprising that only a single TSDC peak is recorded even after repeated observations, as two proton vacancies are normally expected around each Cu^{2+} impurity ion. This can be explained as follows.

The hydrogen bond in maleic acid is less stronger than the hydrogen bond in the

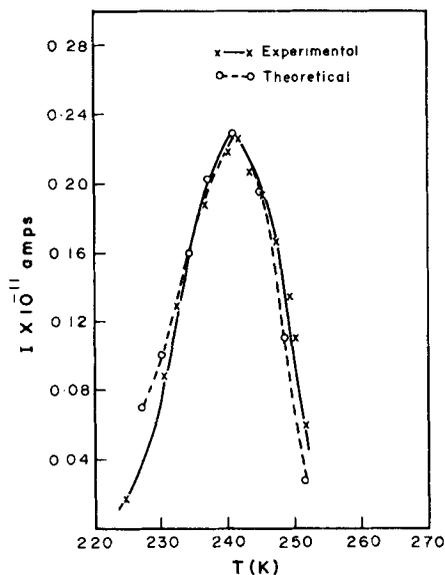


Figure 7. TSDC spectrum of KHM:Cu²⁺ · $T_p = 303$ K and $E_p = 250$ V.

Table 2. Activation energies E and frequency factor $1/\tau_0$ of KHM:Cu²⁺ from TSDC studies.

T_m (K)	Method	E (eV)	$1/\tau_0$ (sec ⁻¹)
241	Cuve fitting	0.65	1.035×10^{26}
	Chen	0.63	
	Nomogram	0.64	

hydrogen maleate (HM⁻) ion. There are two such hydrogens on either side of the mirror plane (figure 1) in each maleate ion. When Cu²⁺ enters the lattice interstitially, it is more probable that these two hydrogen atoms are removed to affect charge compensation. In the case of i.v reorientation, these two vacancies would have almost the same frequency and activation energy resulting in a single peak. Such a reorientation in N₂H₆SO₄ crystals is observed from NMR experiments (Harrell and Peterson 1975). Here two NH₃ dipoles reorient almost with the same activation energy and relaxation time.

The frequency factors $1/\tau_0$, determined are of the order of 10^{26} sec⁻¹ in KHM:Cu²⁺. Such high values are observed in the present study and also in the case of Li(N₂H₅)SO₄:VO²⁺ (Reddy *et al* 1982a). However, in the literature, values of frequency factors upto 10^{19} sec⁻¹ are reported in ionic crystals (Radhakrishna and Haridoss 1978). Whenever very high values are observed, the physical significance of the attempt to escape frequency is lost. However, the present values may be related to the molecular rotations in the crystals.

The conductivity results on pure and doped systems, the TSDC experiment and the sign of the charge carriers given by TEP measurements indicate that protons are most probably the charge carriers in KHM. However, a coulometric experiment performed on this crystal, as described by Reddy *et al* (1982b) could not evolve observable gas,

presumably because the crystal has very high resistivity at room temperature and direct evidence for proton conduction could not be established.

Acknowledgements

One of the authors (ADR) is thankful to UGC, New Delhi for financial assistance. The authors thank Dr V Chandra Mouli for suggesting the crystal.

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